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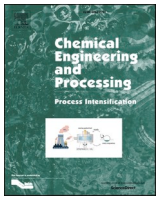

# Current status and future trends of computer-aided process design, applied to purification of liquid biofuels, using process intensification: A short review

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ABSTRACT

Biorefineries offer very interesting challenges and opportunities associated with the separation and purification of complex biomass components. Separation and purification processes can account for a large fraction of the total capital and operating costs. Significant improvement in separation and purification technologies can greatly reduce overall production costs and improve economic viability and environmental sustainability. Process intensification is a valuable strategy to enhance the performance of production processes. It may allow reductions in costs and environmental impact, and enhancements in terms of operability and safety. Although the PI philosophy and methodology have a relatively long history in the scientific field, the ideas of this philosophy fit well with the current trends of sustainability and circular economy; since both ideas, in short, seek the reduction of resource use, the reduction of waste, and the continuous and circular use of raw materials. To ensure the sustainability of the purification of biofuels, it is important to develop processes with low environmental impact, which can also be allowed through the development of intensified technologies. In this paper, advances on aided process design applied to the purification of liquid biofuels using Process Intensification are presented. Trends and challenges are discussed, together with the main opportunity areas.

## 1. Introduction

World consumption of marketed energy is expected to increase by 71% over the 2003–2030 period, with demand nearly tripling in Asia to power the projected increase in economic growth [118]. In the area of marketed energy use, fossil fuels, especially oil, continue to be the dominant energy source. The world energy demand was $5.5 \times 10^{20}$ J in 2010 [29]. The studies predict an increase of a factor of 1.6 to reach a value of $8.6 \times 10^{20}$J in 2040 [12]. The oil demand is mainly driven by the transport and industry sectors [29]. The transportation sector, which accounts for a quarter of the world's energy and global carbon dioxide emissions, also accounts for one-half of the total projected increase in oil use between 2003 and 2030 [29]. The proved oil reserves are concentrated in a few regions in the world. Supply security and risk abatement are the key drivers behind looking at alternatives to oil across the globe. Considering the meager oil reserves, it is crucial to look for diversification of energy sources to reduce the dependency on oil [31]. On the other hand, as climate change becomes an issue of ever-stronger concern in the world, stronger efforts are being devoted to tackling this issue. The International Energy Agency (IEA) has recently proposed the 2 °C scenario (2DS) as a way to handle the climate change issue. The 2DS scenario requires that carbon dioxide ($CO_2$) emissions in 2060 should be reduced by 70% in comparison to the 2014 level [52]. The transport sector plays an important role to achieve this goal considering that the transportation sector is responsible for about 23% of total $CO_2$ emissions [52]. The European transport sector was responsible for more than 25% of the European Union total greenhouse gas emissions (GHG) in 2017 and 31% of energy consumption [29]. In 2017, road transport was responsible for 72% of GHG emissions from transport [99]. Although electricity has been considered as a promising option for reducing $CO_2$ emissions in transportation [133], transport biofuel is estimated to be the key alternative energy in the transport sector. The share of biofuels in total transportation-fuel consumption by 2060 is predicted to be 31%, followed by electricity at 27% based on the mobility model results of IEA for the 2DS [52]. Biofuels production must be increased by a factor of 10 to achieve this goal [87]. Further, world energy demand will continue

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increasing. The bioenergy delivery potential of the world's total land area excluding cropland, infrastructure, wilderness, and denser forests is estimated at 190 × $10^{18}$ J yr-1, 35% of the current global energy demand [42].

In general, biofuel may refer to any form of fuel derived from biomass, and accordingly, its application can be in household energy (cooking and heating), for electricity generation, or in the transport sector. The term biofuel in this paper specifically refers to those biomass-derived fuels that can be used in the transport sector such as bioethanol, biodiesel, biobutanol, among others. Currently, bioethanol and biodiesel account for more than 90% of global biofuel use [99]. The European Union is promoting the use of biofuels, primarily due to the savings of GHG emissions that biofuels can potentially offer. Biofuels can diversify the offer of transport fuel and are a way to raise energy self-sufficiency, diversify the production sites, and strengthen the internal agriculture of a country. Lastly, they are suitable, in many cases, for being used in current power trains and fuel infrastructures [30].

Biomass is an attractive energy source for several reasons. First, it is renewable as long as it is properly managed and second, it is also more evenly distributed over the earth's surface than are finite energy sources and may be exploited using more environmentally friendly technologies. Biomass provides the opportunity for increased local, regional, and national energy self-sufficiency across the globe. The energy in biomass can be accessed by turning the raw materials, or feedstocks, into a usable form. Transportation fuels are made from biomass through biochemical or thermochemical processes [118]. Known as biofuels, these include ethanol, butanol, biodiesel, and biojet fuel, among the most relevant.

Biomass contributed around 4532 trillion BTU in 2020, or about 4.5 quadrillions Btu, or about 4.9 percent of total primary energy consumption in the United States [99]. Approximately 2101 BTU came from wood and wood-derived biomass, 2000 BTU came from biofuels (mostly ethanol), and 430 BTU came from municipal waste biomass [99].

According to [12], in 2020, the United States was the world's largest biofuel producer, with a production of 1347 petajoules. Brazil and Indonesia were placed second and third, respectively, with 884 and 283 petajoules. Germany, on the other hand, produced about 146 petajoules of biofuel in that year, placing the country among the top five biofuel producers in the world and the leading producer in Europe (see Fig. 1).

The United States is by far the world's greatest biofuel producer, accounting for 38% of worldwide biofuel output in 2019 [12]. This year, the country generated 1557 petajoules and is a major biodiesel producer. From 187 thousand barrels of oil equivalent per day in 2000 to 1.8 million barrels of oil equivalent per day in 2019, global biofuel output has steadily grown [52].

Biofuels, in conjunction with their positive carbon balance with regards to fossil fuels, also represent a significant potential for sustainability and economic growth of industrialized countries because they can be generated from locally available renewable materials. Biofuels are usually classified as follows [7]:

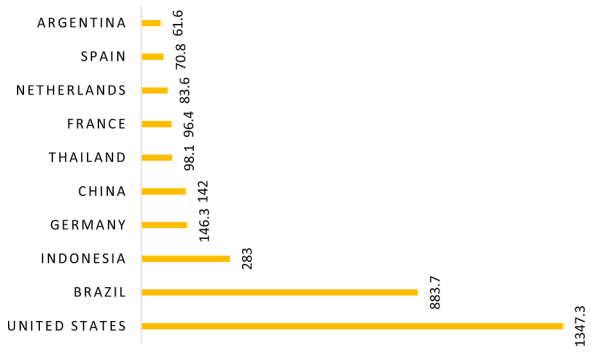


**Fig. 1.** Leading countries based on biofuel production worldwide in 2020 (Production in PetaJoules). Data were taken from [12].

1 First-generation biofuels (1 G) are directly related to biomass that is generally edible.
2 Second-generation biofuels (2 G) are defined as fuels produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes.
3 Third-generation biofuels (3 G) are, at this point, related to algal biomass but could to a certain extent be linked to utilization of $CO_2$ as feedstock.
4 Fourth-generation biofuels (4 G) are genetically engineered. Though 4 G is still in the experimental laboratory stage, it is being developed from the modification of algae. In this way, algae are being metabolically modified to have higher oil contents, increased carbon capture capability, and enhanced cultivation, harvesting, and fermentation procedures

Biofuels are frequently utilized as additives or as part of mixes with fossil fuels. The national army is one of the major users of biofuels in the United States. Blends having up to 10% ethanol can be used in a variety of automobiles [31]. Many Ford T models ran on ethanol around the turn of the twentieth century. Biofuels can also be produced by consuming or converting biomass. Thermal, chemical, or biological conversions are all possible. In 2019, the United States consumed 4985 trillion British thermal units of biomass [31].

In contrast to the 187 thousand barrels of oil equivalent per day produced in 2000, global biofuel output reached 1677 thousand barrels of oil equivalent per day in 2020 [52]. Policies encouraging the use and production of biofuels have fueled growth, with the belief that they may offer energy security and reduce greenhouse gas emissions in key industries. Biofuels can be advantageous since they have fewer environmental consequences than fossil fuels and they use waste materials that would otherwise be wasted. The biofuel industry has been influenced by blending requirements, sustainability objectives, fuel quality standards, and import taxes. The global biofuel production since 2001 can be referred to in the BP Statistical Review of World Energy (2021) in Table 1. By 2024, the worldwide biofuels industry is estimated to be worth $153.8 billion US dollars [12].

Bioethanol is in a liquid state and contributes significantly to low carbon dioxide emissions. Conventional car engines have been timed to bioethanol combustibility and successful operation is observed without any extraordinary modifications in design and technology [130]. It has

**Table 1**
Industries to make biofuels.

| Type of biomass | Industry | Industry | Type of biomass | Industry |
|---|---|---|---|---|
| **2G** | Abengoa Bioenergy | KL Energy | **3G** | Aurora Biofuels |
| | Bluefire Ethanol | LanzaTech | | OriginOil |
| | BP Biofuels | Lignol | | PetroAlgae |
| | Choren | Mascoma | | Sapphire Energy |
| | Chemrec | Neste Oil | | Solazyme |
| | Cobalt Biofuels | Petrobras | | Solix |
| | Coskata | POET | | Synthetic Genomics |
| | DuPont Danisco | Praj Industries | | |
| | Dynamotive | Qteros | **4G** | Algenol |
| | Enerkem | Range Fuels | | Amyris Biotechnologies |
| | Fulcrum Bioenergy | Rentech | | Joule Unlimited |
| | Gevo | Terrabon | | LS9 |
| | Inbicon | TMO Renewables | | Naturally Scientific |
| | IneosBio | Verenium | | |
| | Iogen | Virent | | |
| | | ZeaChem | | |

high octane number, greater anti-knocking activity, and is suitable to use as an additive for gasoline and fuel itself, with E85 (85% ethanol) assuring maximum engine efficiency (Balat et al., 2008). In contrast to gasoline, ethanol has low volumetric energy density and requires 50% more volume than gasoline to cover the same distance [31]. Ethanol being water-soluble shows severe corrosion of mild steel and aluminum surfaces within the engine. The corrosion potential significantly depends on the blend ratio of ethanol and gasoline such as the E60 (60% ethanol, 40% gasoline) exhibited the maximum corrosive tendency whereas, no corrosion is found for absolute ethanol, often termed as E100 [108].

Biobutanol is another important fuel and solvent in the paint industry. It is a superior fuel additive owing to its non-hygroscopic properties, maximum blending ability with petroleum, and utility in conventional combustive engines. The earliest commercial production of bio- butanol is reported to start in the late nineteenth century after Louis Pasteur devised Acetone-Butanol-Ethanol oxidative pathway from biological matter (fermentation). With the increasing demand and emergence of low-cost petroleum-based butanol, biobutanol synthesis was considered redundant [109]. The resurgence of butanol of biological origin aligns with a reduction in alarming levels of GHG emissions and mitigation of global climate change. Biobutanol is an alternative to conventional transportation fuels. The benefits of biobutanol include a) higher energy content—biobutanol's energy content is relatively high among gasoline alternatives. However, a) biobutanol's energy density is 10%–20% lower than gasoline's energy density; b) lower vapor pressure—when compared with ethanol, biobutanol has a lower vapor pressure, which means lower volatility and evaporative emissions; c) increased energy security—biobutanol can be produced domestically from a variety of feedstocks; d) fewer emissions are generated with the use of biobutanol compared with petroleum fuels; e) more transport options—biobutanol is immiscible with water, meaning that it may be able to be transported in pipelines to reduce transport costs [101, 103].

One of the major biofuels is biodiesel that is obtained from the transesterification reaction of alcohol with fatty acids obtained from animal, vegetable oil, or algal oil [73]. It is an environment-friendly fuel, as it reduces 75% $CO_2$ emissions in comparison to diesel obtained from crude oil. The physical properties of low combustibility, crystallization at low temperature, and high viscosity render its social and economic importance [59]. These parameters are controlled by blending with other fuels like B2 (2% biodiesel and 98% organic diesel) and B5 (5% biodiesel and 95% diesel) blends, preheated fuel intake, and auxiliary electrical heaters in engines [59]. Besides multiple advantages over fossil fuels, biodiesel is also found to have some adverse effects on the environment associated with seedling germination, biodiversity, and physiochemical characteristics of soil [5].

Finally, bio-aviation fuel (also known as biojet fuel, renewable jet fuel, or aviation biofuel in some literature), a type of biofuel for the air transport sector, is recognized as a short- to medium-term solution toward an overall reduction of the sector's GHG emissions. Biojet fuel is a biomass-derived synthesized paraffinic kerosene (SPK) that is blended into conventionally petroleum-derived jet fuel [106]. The hydro processed esters and fatty acids production pathway (HEFA), an oil-to-jet production platform, produces HEFA-SPK via the deoxygenation of oils and fats followed by hydroprocessing. In the alcohol-to-jet production platform or pathway (ATJ), biomass is hydrolyzed to produce fermentable sugars, the sugars are fermented to produce alcohols, and then they are dehydrated, oligomerized, hydrogenated, and fractionated to produce ATJ-SPK. More novel processes can convert sugars directly to hydrocarbons [43]. Aviation fuels are subject to strict compositional requirements beyond those required for road transport fuels. A high energy density is a key requirement as well as attributes such as lubricity and cold flow properties. To ensure the required properties are achieved biojet is currently blended with fossil fuel-derived jet fuel [46]. In summary, Table 1 shows some industries that produce biofuels of second, third, and fourth generation.

Biomass can be converted into liquid biofuels via biorefinery technologies. A biorefinery is a facility that integrates biomass conversion processes to produce fuels, power, and chemicals from biomass. The biorefinery economy is a vision for a future in which biorenewables replace fossil fuels. The transition to a biorefinery economy would require a huge investment in new infrastructure to produce, store, and deliver biorefinery products to end-users [21]. There are four main biorefineries: biosyngas-based refinery, pyrolysis-based refinery, hydrothermal-based refinery, and fermentation-based refinery. Combining higher value products with higher heating value fuels production and employing any combination of conversion technologies has the greatest potential for making fuels, chemicals, and materials, and power from biomass competitive. Obtaining modern biofuels, biopower, and bioproducts from biomass can be realized only in the integrated biorefineries. Biorefineries too will use only those technology platforms that are most cost-effective for converting a certain type of biomass into a certain collection of desired end products. The sustainability of a biorefinery depends on the comprehensive utilization of the biomass feedstock to give a diverse product portfolio. This would only be possible with an optimal mix of processes [91]. A full realization of the utilization potential of any biomass resource often requires a complex set of operations. Besides the actual chemical transformation steps, a multitude of physical processes is involved in the raw material pretreatment as well as in the separation of intermediates and products [37]. Therefore, for a biorefinery to be sustainable and economically competitive with an oil refinery, it must present low energy consumption, low operating costs, low environmental impacts, inherent safety, and good dynamic behavior in the design and operation of all equipment. For this reason, it is essential to implement strategies that aim to achieve these key objectives in the design of a biorefinery that produces liquid biofuels [23].

Increasing awareness for energy sustainability, environmental concerns, new and unconventional feedstocks, as well as recent advances in process optimization have sparked a renewed interest in process intensification (PI). PI aims to drastically reduce the energy consumption and processing cost of the chemical processes by utilizing the synergy between multifunctional phenomena at a different time and spatial scales and enhancing the mass, heat, and momentum transfer rates. There has been significant growth in the field of process intensification over the past decades that featured both successful industrial applications and increased research interest in academia [22, 124].

Ponce-Ortega et al. [98] defined PI as any activity aiming at the following five outcomes:(a) smaller equipment size for a given throughput; (b) higher throughput for a given equipment size or a given process; (c) less hold up in equipment or less inventory in process for the same throughput; (d) less usage of utility materials and feedstock for a given throughput, and (e) higher performance for given unit size. This definition regarded PI as an extension of process integration activities. Based on this, they summarized the potential benefits of PI activities as realizing cheaper, safer, more energy-efficient, and/or more environmentally friendly processes through innovation while valuing customers through just-in-time manufacturing.

Process intensification can be accomplished from different perspectives integrating/hybridizing various levels of abstraction [40]:

- Integration of known unit operations: hybrid reaction-reaction, reaction-separation, or separation-separation systems.
- Integration of functions: incorporate new functionality into a known operation based on the bioprocess limitations.
- Integration of phenomena: identify target key phenomena to accomplish biotransformation and customize the bioprocess design to put them together.

Yong et al. [134] have summarized the future trends of the sustainable development of energy systems in three main areas: (i) higher efficiency and waste reduction of biofuel production, (ii) $CO_2$ removal and conversion, and (iii) process integration. Concerning process integration, Nemet et al. [84] have noted that the scope of PI is becoming

much wider, considering the integration of not only heat and power but also water, safety, and other aspects of processes. To date, most of the research in biorefineries focus on the conversión or pretreatment aspects, whereas the real cost of biorefineries remains in the downstream processing, which can account for up to 60 – 80% of the total cost production [65, 104]. In this sense, biorefineries can become viable and sustainable only by using intensified separations that allow the low-cost and high-volume production of biofuels. In addition to the biomass conversion processes, separation and purification of the biomass components and the products streams and their full integration with the overall process is of utmost importance. In many instances, this can be the single biggest factor influencing the overall success and commercialization of biorefineries. Given the significance and importance of this area, separation and purifications technologies and their applications in the production of liquid biofuels is the focus of this paper. This paper highlights the importance of process intensification in the purification of liquid biofuels (bioethanol, biobutanol, biodiesel, and biojet fuel) and discusses the required interdisciplinary approach to accomplish it. We outline intensified separation technologies reported in the literature and current challenges of processes intensification in the purification of those liquid biofuels at different levels. We present an overview of important ideas addressed within methodologies proposed for designing intensified processes.

## 2. PI in the bioethanol purification

Bioethanol is mixed with gasoline according to many countries' legislation pursuing environmental sustainability by reducing the use of fossil fuels (E5, E10, E15, etc.). Bioethanol is produced by fermentation of much organic waste or biomass resources in diluted aqueous media. Unfortunately, bioethanol for fuel use must have a low content of water and its recovery is an energy-intensive operation [96]. The highest purity obtainable with conventional separation procedures is limited by the development of a homogenous minimum-boiling azeotrope at 95.6 percent by weight concentration of ethanol at 78.15 C and 101.3 kPa.

Therefore, the principal problem in the production of anhydrous bioethanol (> 99 mol%) is the high energy cost involved in its separation. During the fermentation stage, large quantities of fermentation broth are obtained with low concentrations of alcohol (between 5 and 12% by weight) so it is necessary to eliminate excess water. According to Fig. 2, the conventional method for the recovery of anhydrous bioethanol from the fermentation broth contain at least three stages [116]:

- Conventional distillation (PDC, Fig. 2) of dilute ethanol to a concentration close to its azeotropic point (95.57% by weight).
- Extractive or azeotropic distillation (EDC, Fig. 2) using a third component to break up the azeotrope and remove the remaining water. Extractive distillation performs the separation in the presence of a relatively non-volatile, high-boiling, and miscible component that does not form an azeotrope with the other components of the mixture. For bioethanol-water extractive distillation, ethylene glycol continues to be the most widely used entrainment agent, although glycerol, hyperbranched polymers, and ionic liquids have also been proposed.
- Distillation to recover the third component and reuse it in the process (SRC, Fig. 2).

The recovery of bioethanol by these methods implies the consumption of 50 and 80% of the total energy required in the entire bioethanol production process through fermentation [116]. The recent interest in the search for clean and economic processes, and the strengthening of environmental legislation that restricts the use of solvents such as those used in azeotropic and extractive processes has led the industry to focus on other intensified technologies. The intensification of processes has been a tool that has supported the different proposals for the sustainable purification of bioethanol [112]. Several studies presented energy and cost reduction for the bioethanol production process; however, the research areas have been predominantly restricted to the dehydration unit.

### 2.1. Using thermally coupled and internally heat-integrated distillation options

The most popular intensified schemes, based on thermal coupling, for the purification of bioethanol, are the thermally coupled extractive distillation column (Fig. 3) and the extractive dividing wall column (Fig. 4). Reported studies reveal that thermally coupled extractive distillation systems provide energy reduction in comparison with conventional distillation columns [13, 47].

In a pioneering paper by Hernández [49], three complex extractive distillation options were studied for the purification of a dilute mixture of ethanol and water. The first option uses an extractive distillation column and the other two options use thermally coupled extractive distillation sequences. The results indicate that the fully thermally coupled extractive option can reduce energy consumption by 30% compared to the scheme that uses an extractive distillation column. This fully thermally coupled extractive distillation sequence can produce ethanol as distillate with a mass fraction of 0.995, the entrainer as bottoms product, and a mixture of ethanol and water as the sidestream.

Sun et al. [122] investigated the design and optimization of a dividing wall column for heterogeneous azeotropic distillation using cyclohexane as a solvent, starting from the near-azeotropic feed of ethanol and water. Simulation results indicate that the azeotropic dividing wall column has thermal energy savings of 42% and 35% lower total annual cost over azeotropic conventional distillation sequence using cyclohexane as solvent. Also, the azeotropic dividing wall column eliminates the back-mixing of ethanol thus improving thermodynamic efficiency by 1.57%.

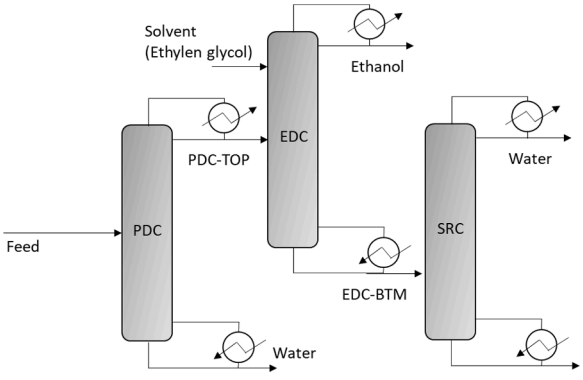


**Fig. 2.** Conventional process for bioethanol purification.

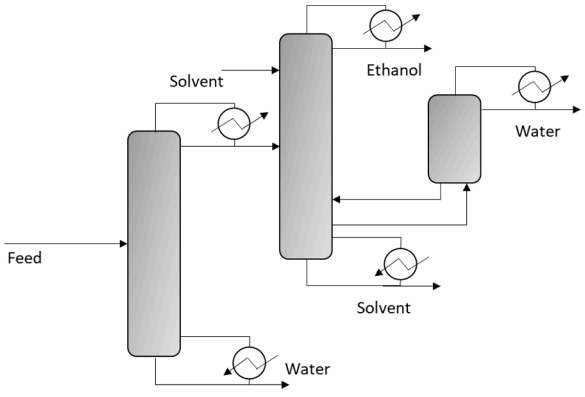


**Fig. 3.** Thermally coupled extractive distillation Scheme.

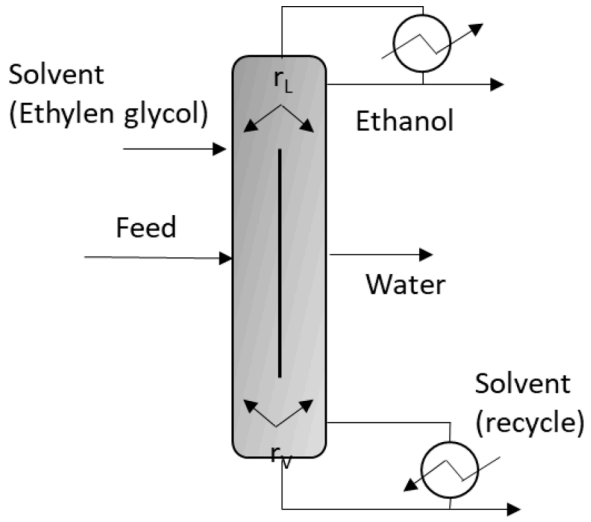


**Fig. 4.** Extractive dividing wall column.

The modeling, simulation, and control of an internally heat integrated pressure-swing distillation process to separate the ethanol/water azeotropic binary system into a high purity ethanol stream are addressed in the work of Mulia-Soto and Flores Tlacuahuac [82]. Despite the high interaction between the column sections, the results show that the proposed separation process can be operated smoothly with an array of PI controllers. Moreover, the purity of ethanol is maintained with the control structure proposed in the face of upsets.

Kiss and Suszwalak [62] proposed novel distillation technologies for enhanced bioethanol dehydration by extending the use of dividing wall column to azeotropic distillation sequence (using pentane as solvent) and extractive distillation configuration respectively. Azeotropic and extractive designs and their corresponding alternatives based on dividing wall columns are optimized using SQP. The optimized Extractive and azeotropic configurations with dividing wall columns lead to thermal energy savings of 10% and 20% over conventional arrangements (using pentane as solvent) respectively.

Kiss and Ignat [61] proposed extensions to the conventional extractive dividing wall column studied by Kiss and Suszwalak [62] for bioethanol dehydration such that separation is performed in a single dividing wall column. In other words, the proposed configuration integrates all the three columns of conventional distillation sequence into a single dividing wall column. Both conventional distillation sequences into an extractive dividing wall column are optimized for a minimum energy requirement using sequential quadratic programming. Extractive dividing wall leads to a 17% reduction in energy requirement and 16% in total annual cost over conventional distillation sequence.

The availability of intensified distillation sequences for the separation of pure ethanol from the fermentation broth is considered in the paper by Errico and Rong [25]. Extending the concept of thermally coupled structures and column sections recombination, already successfully applied to ideal mixtures, it was possible to generate new distillation sequences for azeotropic mixtures. The new intensified arrangements are proved to have a lower energy consumption together with a reduced capital cost compared to the classical sequence proposed in the literature. Furthermore, Ramírez-Márquez et al. [105] established that those novel intensified configurations provide operational advantages compared to traditional conventional schemes.

Tututi-Avila et al. [125] studied the design and control of the extractive dividing wall column, with the dividing wall in the top part of the column, an alternative to conventional extractive distillation sequence for bioethanol dehydration to 99.5 wt% ethanol. The process using a feed of 93 wt% ethanol in water is simulated in Aspen Plus. The above two sequences are optimized using the genetic algorithm coupled with Aspen Plus. The optimal extractive dividing wall column results in 12.4% savings in TAC over conventional extractive distillation configuration.

Tututi-Avila et al. [125] studied the design and control of the extractive dividing wall column, with the dividing wall in the top part of the column, an alternative to conventional extractive distillation sequence for bioethanol dehydration to 99.5 wt% ethanol. The process using a feed of 93 wt% ethanol in water is simulated in Aspen Plus. The above two sequences are optimized using the genetic algorithm coupled with Aspen Plus. The optimal extractive dividing wall column results in 12.4% savings in TAC over conventional extractive distillation configuration.

The inclusion of thermal coupling in conventional distillation sequences and the use of thermally coupled columns led to reducing total annual cost in the bioethanol dehydration process when compared to the sequences without this thermal integration according to the work of Brito et al. [14].

Torres Ortega and Rong [126] proposed replacement of flashes by column sections, hybridizing unit operations by reformulating column sections, and relocation of column sections as novel synthesis approaches to formulate hybrid units and divided wall columns between the bioethanol recovery and purification obtained by lignocellulosic fermentation broth. The new intensified alternatives achieved relevant savings, ranging from 17 to 23% in TAC (total annual costs), and ranging from 18 to 28% in TEC (total energy consumption). Moreover, the reduction of the number of separation units varied from the original eight units down to three units. The intensified system obtained cost savings of 15–20% higher than the multi-effect scheme.

The energy optimization of thermally coupled distillation sequences for the purification of bioethanol using glycerol as entrainer, was analyzed in the paper by Oseguera-Villaseñor [90]. The energy optimization revealed a region where three solutions for the heat duty supplied to the reboiler can be found. As reported in the literature, these multiplicities are found in binary distillation and complex reactive distillation columns. These multiplicities can be attributed to nonlinearities in the model, physical properties, and interactions between the reaction and the separation. This finding is important since we are interested in detecting the optimal energy consumption to reduce the environmental impact caused by the usage and production of energy from petroleum.

Regarding the use of distillation with thermal coupling and dividing wall column in the dehydration process of bioethanol, it can be concluded that thermal coupling of columns reduced the process energy requirement and capital costs by 49%and 17%, respectively. In contrast, the application of the dividing-wall column saved 67% of energy demand, and 19% of expenses compared with the base case without column heat integration. The results indicated that applying the mentioned intensified methods plays an essential role in optimizing the separation system [11].

### 2.2. *Using reactive distillation*

Although progress has been made in reducing the energy requirements in the preceding technologies for dehydration of bioethanol, there is still much to be resolved and to overcome the drawback of energy-intensive relevant to distillation columns and breaking the azeotrope ethanol-water. Reactive distillation consists of both reaction and distillation in a single column, in which reactants get converted to products, which are separated in the same column. This process has advantages over the conventional one such as energy-efficient, solvent consumption, capital cost (because fewer number types of equipment are required), and removal of hot spot problems by liquid evaporation [113]. The application of reactive distillation is constrained by operating conditions viz. temperature and pressure and difficulties in proper residence time characteristics. Reactive distillation shows good energy savings for the systems in which the reaction is fast and the reaction

temperature is suitable for separation [114]. In recent years, studies have been reported that apply the reactive distillation method, which combines reaction and distillation processes in a single column for the dehydration of bioethanol.

A novel approach to removing water from near-azeotropic ethanol-water mixtures is proposed based on the hydration of ethylene oxide to produce ethylene glycol in a reactive distillation column in the work of An et al. [2]. Steady-state simulations were carried out to investigate the feasibility of the suggested approach, and a sensitivity analysis was carried out to obtain the optimal design parameters. The results showed that using the optimal operating conditions, a reactive distillation column is capable of circumventing the azeotropic limitation to obtain anhydrous ethanol. Compared with traditional approaches, the proposed approach is promising because of its great potential for reducing energy consumption and capital costs. In a complementary study, Tavan and Hosseini [123] establish that the optimum number of reaction trays is 17 and introducing both feeds to the 13th stage leads to minimum energy demand.

An enhanced process configuration is economically evaluated and dynamically controlled based on the idea of consuming the water by reacting it with ethylene oxide to produce ethylene glycol, in the paper of Kaymak [55], thus obtaining pure bioethanol by breaking the water-ethanol azeotrope without adding any separation agent. Design results show that reactive distillation is an attractive option because it outperforms the base-case design (only distillation columns) by a 19.3% decrease in total annual cost. In addition, it generates an economic income by producing ethylene glycol as an added-value byproduct.

Guzmán-Martínez et al. [48] present, via simulation, economic and environmental comparison of alternative methods for ethanol dehydration based on ethylene oxide/propylene oxide hydration and azeotropic distillation with benzene and cyclohexane. These reactive methods consist of conventional reaction separation processes and intensified processes such as reactive distillation, both coupled with organic Rankine cycles, offering an additional value-added product (ethylene glycol or propylene glycol), electric power generation, and the capacity to reduce the global process steps in anhydrous ethanol production. The results indicate that reactive dehydration, specifically the reactor–separator process using propylene oxide at a low ethanol concentration is the best economic and environmental option among all the processes studied for anhydrous ethanol production.

Reactive distillation and membrane-assisted reactive distillation have been considered as possible alternatives to extractive distillation for the concentration of ethanol from diluted streams by Errico et al. [28]. Different alternatives were proposed where the pre-concentration step was performed by membrane stand-alone or a combination of membrane and ordinary distillation. In all the configurations reactive distillation using ethylene oxide was considered to reach the ethanol final concentration of 99.9 wt%. It was obtained that ordinary distillation coupled with reactive distillation is at the moment the only alternative competing with extractive distillation. However, the sequence of membranes, ordinary distillation, and reactive distillation have clear potentials to compete with the stand-alone distillation processes once the solutions for draw recovery and minimization of ethanol loss will be available.

Regarding the use of reactive distillation for the dehydration of bioethanol, the results show that the reactive distillation process has some advantages in terms of operating and capital investment costs and this process can be used for large biorefineries in the production of biofuels with high overall efficiency.

### 2.3. Other intensified alternatives

The separation strategy for systems of various com positions into products with preset quality is dictated by the existence of azeotropy in the ethanol-water system. This strategy involves methods of separation of azeotropic mixtures (azeotropic, heteroazeotropic, and salt effect distillation techniques; distillation combined with phase separation; pressure swing distillation among others), which are aimed at circumventing thermodynamic limitations and are based on the principle of concentration field redistribution between distillation regions. However, few applications based on process intensification have been developed under these ideas.

Avilés-Martínez et al., [6] have proposed, for the purification of a typical mixture of ethanol/water obtained from the fermentation of biomass, several hybrid configurations. This study proposes alternative hybrid systems using liquid-liquid extraction and extractive distillation. The use of n-dodecane as entrainer for liquid-liquid extraction and glycerol as entrainer for extractive distillation has been considered. The proposed systems are analyzed and a comparison is done on their performance in terms of energy and total annual cost. It has been found that the hybrid scheme presents both lower total energy consumption and lower total annual cost as compared to the traditional purification scheme with conventional distillation and extractive distillation. In the same line, Vázquez-Ojeda et al. [131] present the design and optimization of a dehydration process for ethanol, using two separation sequences: a conventional arrangement and a hybrid arrangement based on liquid-liquid extraction. Three extraction solvents were evaluated for the hybrid design: octanoic acid, octanol, and ethyl hexanol. The results show considerable savings in total annual cost (32% approximately) for the hybrid systems, for a feed stream with 10% mol (22 wt%) of ethanol.

A techno-economic analysis for the separation process in bioethanol production is presented in the paper by Vázquez-Ojeda et al. [130]. Process integration improves significantly the separation process because it helps to reduce the overall energy required in the reboilers based on energy integration and additionally to diminish the amount of required solvent based on mass integration. The SYNHEAT optimization model was applied for energy integration whereas a direct recycle strategy was implemented for the mass integration process. The best separation processes obtained correspond to an integrated hybrid separation sequence with energy integration with significant savings in utility costs and possible recycling of nearly all solvents.

Two processes for recovery and purification of bioethanol from fermentation broth are studied and compared consistently after heat integration and optimization in the paper by Loy et al. [72]. One is pressure swing adsorption, which is commonly employed in the industry, and another is the extractive dividing wall column which is currently of research interest since it can potentially reduce capital and energy costs. Results indicate that, while extractive dividing wall column has advantages over pressure swing adsorption in terms of capital cost and thermal energy demand (results agree with the anticipated benefits and results reported by Kiss and Ignat in 2013 [63]), pressure swing adsorption still has 33% lower cost of manufacture per unit product than extractive dividing wall column, mostly because of solvent loss. This shows that it is not sufficient to consider only energy requirements in assessing the feasibility of a promising intensified technology; rather, an overall economic evaluation under realistic conditions should be performed.

Cyclic distillation is an intensified method based on separate phase movement that leads to key advantages: increased column throughput, reduced energy requirements, and better separation performance. The work by Maleta et al. [76] is the first to report the performance of a pilot-scale distillation column for bioethanol-water separation, operated in a cyclic mode. A comparative study is made between a pilot-scale cyclic distillation column and an existing industrial beer column used to concentrate bioethanol. Using specially designed trays that truly allow separate phase movement, the practical operation confirmed that 2.6 times fewer trays and energy savings of about 30% are possible as compared with classic distillation

A heterogeneous azeotropic dividing-wall column is proposed by demonstrating ethanol dehydration in the work by Li et al. [68]. Overall assessment of the azeotropic dividing-wall column is implemented by comparing the optimal design and dynamic controllability with two

conventional sequences. Significant energy saving of 21.36% and 11.97%, the total annual cost of 18.48% and 18.43% can be obtained compared with conventional azeotropic/recovery sequence and conventional azeotropic/stripper sequence, respectively.

The application of membranes in ethanol recovery after fermentation is presented in the paper by Kumakiri [67]. A preliminary simulation was performed to compare different process configurations to concentrate 10 wt% ethanol to 99.5 wt% using membranes. In addition to the significant energy reduction achieved by replacing azeotropic distillation with membrane dehydration, employing ethanol-selective membranes can further reduce energy demand. The influence of contaminants in the bioethanol on the membrane properties and required further developments are also discussed.

Recently, a hybrid process consisting of distillation and membrane dehydration was proposed as an energy-saving alternative. In the hybrid process, azeotropic distillation was replaced with membrane separation [56]. In the early 2000s, a successful industrial application of A-type zeolite membranes, a type of inorganic membrane, to dry solvents was reported by Morigami et al. [81]. Since then, the number of industrial applications of membrane integrated processes has been growing, and more than two hundred units are under operation today [56].

In the future, new intensified alternatives for bioethanol separation should be studied extensively for an accurate comparison. Intensified processes involving distillation and membrane separations hold promise with the potential to reduce the energy and operating costs of bioethanol separation. Developing these intensified processes will help achieve a sustainable path to bioethanol production. One of greater relevance is the development of membranes with higher ethanol-water selectivity, permeability, greater resistance to fouling, longer life, and lower cost [119].

Finally, Table 2 shows a summary of the amount of energy that some authors report to separate 1 kg of ethanol using intensified technologies.

**Table 2**
Energy requirements for bioethanol purification.

| Feed Stream (water+ethanol) | Energy requirements (MJ/kg ethanol) | Separation Technology | Reference |
|---|---|---|---|
| 100 kmol/h (10% mol ethanol) | 0.68 | Thermally Couple and fully thermally coupled distillation columns | Hernández, S (2008)* |
| 1000 kg/h (10% wt ethanol) | 70.83 | Dividing-Wall Heterogeneous Azeotropic Distillation Column | Sun et al. [122] |
| 100 kmol/h (20% mol ethanol) | 16.8 | Pressure-swing distillation | Mulia-Soto and Flores Tlacuahuac [82] |
| 100 kmol/h (85% mol ethanol) | 1.7 | Extractive and azeotropic distillation in dividing-wall columns | Kiss and Suszwalak [62] |
| 125,000 kg/h (10% wt ethanol) | 7.42 | Extractive distillation | Kiss and Ignat [61] |
| 45.35 mol /h (10% mol ethanol) | 7.37 | Hibrid Processes Liquid-Liquid Extraction/Extractive Distillation | Avilés-Martínez et al., [6] |
| 4313 kmol/h (11.9% wt ethanol) | 7.47 | Extractive distillation | Errico and Rong [25] |
| 45.36 kmol/h (84% mol ethanol) | 1.37 | Extractive dividing-wall column | Tututi-Avila et al. [125] |
| 32,907 kg/h (5% wt ethanol) | 5.32 | Membrane assisted reactive distillation | Errico et al. [28] |

* It is not considered the beer column.

## 3. PI in the biodiesel process

Biodiesel, an environmentally friendly renewable energy source mainly originates from renewable lipid feedstocks. Biodiesel production research is an economic field that helps address the global challenge of insufficient energy resources with the aim of reducing greenhouse gas emissions and promoting sustainable economic growth [16]. Generally, esterification/transesterification of free fatty acids/triglycerides with alcohol applying catalytic (chemical and biological catalysts) and non-catalytic are the principal reactions in prevailing biodiesel production. Among all the catalytic routes, biodiesel production using a chemical catalyst is the most commercialized route due to shorter reaction time and high yield [8]. However, there are some limitations in chemical catalysis such as catalyst recovery and recycling, an excessive amount of alkaline wastewater, and complexity of downstream product purification. Additionally, the chemical catalytic process requires high-quality raw materials to save the process from saponification. Thus high-quality raw materials deliberately affect the process economics and increase the product cost [9].

The conventional reactor-separation flowsheet where transesterification and esterification take place in the reactor and the products are separated in a sequence of distillation columns is a traditional strategy to produce biodiesel as shown in Fig. 5 [36] [35].

The development of new energy sources, new challenging intensified processes for biodiesel production, and the impact of environmental protection has attracted researchers worldwide and encouraged such research.

### 3.1. Conventional reactive distillation

In pioneering papers, a continuous reactive distillation-based process applied to fatty acids has been described by Bock et al. [10] for the manufacture of isopropyl myristate (with properties similar to biodiesel). The set-up consists of two columns. The process makes use of an excess of alcohol, which distillates together with water as the top product. The alcohol is recycled as an azeotrope with water after separation in a second column. The acid catalyst is lost, neutralized, and washed from the final product. In the same line, in 2003, Omota et al [89]. demonstrated that the synthesis of high purity fatty esters (useful as biodiesel) is feasible by reactive distillation using a solid catalyst. A reactive distillation-set up is proposed for the esterification of the dodecanoic acid with 2-ethyl hexanol and methanol, the heaviest and the lightest alcohols in the series C1 – C8. The design ensured selective water removal that shifts the chemical equilibrium to completion and preserving the catalyst activity.

In one of the most cited papers in Adv. Synth. Catal Journal, Kiss et al. [57] investigated solid acid catalysts (for possible applications in reactive distillation) for fatty acids esterification. Various solid acids (zeolites, ion-exchange resins, and mixed metal oxides) are screened as catalysts in the esterification of dodecanoic acid with 2-ethyl hexanol, 1-propanol, and methanol at 130 - 180 8C. The most promising candidate is found to be sulfated zirconia. The catalyst's stability towards thermal decomposition and leaching is tested and the effects of the surface composition and structure on the catalytic activity are discussed. da Silva et al. [20] presented an efficient process using reactive distillation columns applied to biodiesel production from soybean oil and bioethanol. The key variables affecting the biodiesel production process are catalyst concentration, reaction temperature, level of agitation, ethanol/soybean oil molar ratio, reaction time, and raw material type. The experimental design was used to optimize the catalyst concentration and the ethanol to soybean oil molar ratio.

An integrated heterogeneous two-step reactive distillation process for biodiesel production has been developed in the paper by Pérez-Cisneros [93]. The conceptual design of the reactive distillation columns was performed through the construction of reactive residue curve maps in terms of elements. The design of the esterification reactive distillation

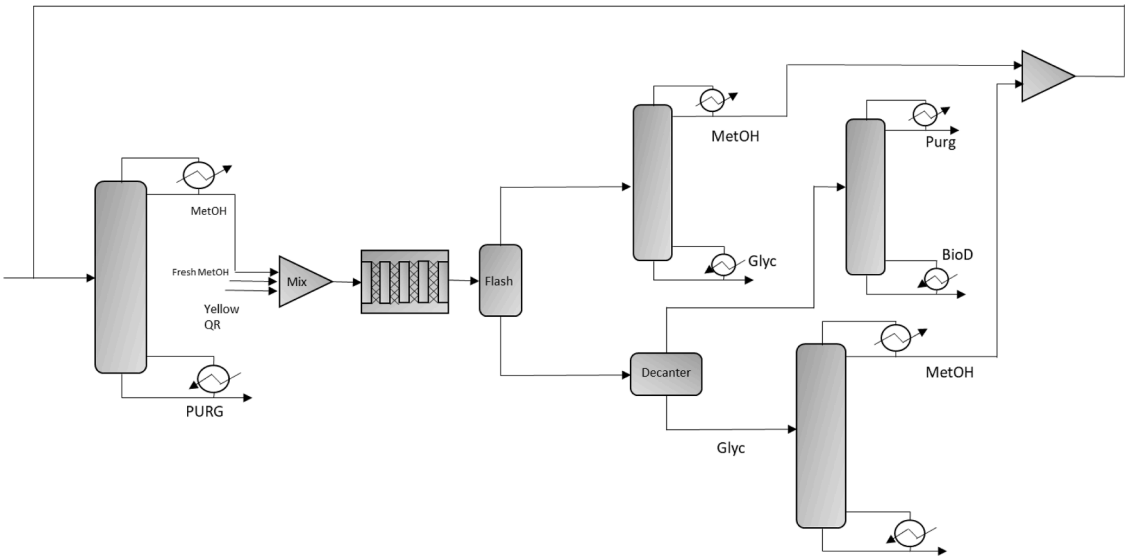


**Fig. 5.** Conventional process for biodiesel production.

column consisted of one reactive zone loaded with Amberlyst 15 catalyst and for the transesterification reactive column, two reactive zones loaded with MgO were used. Results showed that the amount of fatty acids in the vegetable oil feed plays a key role in the performance (energy cost, catalyst load, methanol flow rate) of the integrated esterification–transesterification reactive distillation process.

A novel hybridization of esterification and transesterification processes in a single reactive distillation column was proposed for biodiesel production from waste cooking oil in the paper by Petchsoongsakul et al. [94]. Continuous process operation was designed in a single reactive distillation column using two different types of heterogeneous catalyst. The hybridized process via reactive distillation could reduce the number of equipment, methanol to oil in feed, and energy consumption compared to the conventional alkaline catalyzed process and the process of two reactive distillation columns in series. Net specific energy requirement was achieved to the lower value as 216 kWhr/kmol biodiesel.

Two reactive distillation processes using soybean oil as main feedstock along with the corresponding downstream separation units are simulated in the paper by Poddar et al. [97]: the first process involves a homogeneous alkali catalyst; whereas the second involves a heterogeneous catalyst. Both processes yield a high purity biodiesel product. The energy requirements of both processes were evaluated based on the optimization of the distillation column duties and performing heat integration on the process streams. The optimization of the column duties was performed by analyzing the Column Grand Composite Curves. The results show that the heterogeneous-catalyzed process is more profitable than the alkali-catalyzed process for biodiesel production.

In the study by Joda and Ahmadi [54] a conventional and improved biodiesel production plants have been simulated. The improved process converts waste cooking oil using a reactive distillation catalyzed by a heterogeneous catalyst in which catalyst removal and neutralization units are not necessary. Using pinch technology and exergoeconomic analysis, exergy destruction of each process is calculated and the best configuration to integrate biodiesel production process with a combined cycle power plant is presented. The results show that the produced electricity in the modified process is less expensive.

For the first time, a series of pilot-scale reactive distillation experiments were conducted using the cation-exchange resin catalysts and used for biodiesel synthesis from esterification of soybean oil deodorized distillate with methanol in the work by Gao et al. [33]. The results demonstrated that the use of this technology increases the conversion of esters to 99% and keeps energy consumption and $CO_2$ emission at a low level. Furthermore, the reactive distillation technology over cation-exchange resin catalysts will open a new path to develop a better process for biodiesel synthesis to reduce the production energy consumption, decrease greenhouse gas emission, and increase the commercial competitiveness of this green fuel.

Mondal et al. [79] present a novel reactive distillation column for the production of algal biodiesel by the use of a heterogeneous nano-catalyst, $Ca(OCH_3)_2$. The elitist non-dominated sorting genetic algorithm is employed to optimize the design of this reactive distillation column to maximize biodiesel purity while minimizing total annual cost and $CO_2$ emissions. In this proposed intensified configuration, a reactive stage is thermally integrated with the reboiler to constitute a side vapor recompressed reactive distillation column. A comparative study is performed to quantify the performance improvement of the proposed side vapor recompressed reactive distillation column over the conventional intensified sequence. It is found that there is a 34.6% reduction in $CO_2$ emissions with a payback period of 4.54 years for the vapor recompression. Hence, the proposed complex intensified sequence is attractive with better performance in terms of energetic, environmental, and economic perspectives.

In general, comparison between the conventional (reactor- separation process) and reactive distillation for the production of biodiesel in terms of the annual production costs and economic indicators such as Return-On-Investment (ROI) and payback period, the results show that intensified process is more economically advantageous than the conventional process due to a much higher ROI, lower payback period, and lower annual cost per unit of biodiesel produced [135].

### 3.2. *Thermally coupled reactive distillation*

A modification of the supercritical process for the production of biodiesel fuel is proposed in the work by Gómez-Castro et al. [38]. The process involves the use of either reactive distillation or thermally coupled reactive distillation. The thermally coupled system shows lower energy consumptions than the reactive distillation column. Expanding the study, a simulation analysis of a biodiesel production process with methanol at high pressure and temperature is presented by Gómez-Castro et al. [39]. The study considers aspects of energy, costs, and environmental impact. Modifications to the original process have been proposed and tested; the modifications proposed consist of the intensification of the esterification section by using reactive distillation systems. The study demonstrates the benefits of using reactive

distillation for the esterification step and discusses the environmental impact of the supercritical production process. It has been found that the intensified alternatives reduce the emissions considerably and, through the reuse of the excess methanol, the emissions level of the supercritical process can be compared to those of the catalytic method.

Miranda-Galindo et al. [78] have studied the design of reactive distillation with thermal coupling (using as a study case the production of fatty esters for use as biodiesel), generalizing the use of a multi-objective genetic algorithm with restrictions coupled to Aspen ONE Aspen Plus. The results obtained in the Pareto front indicate that the energy consumption of the complex distillation sequence can be reduced significantly by varying operational conditions. Trends in the energy consumption, total annual cost, and greenhouse gas emissions of the thermally coupled reactive distillation sequences were obtained.

Nguyen and Demirel [85] presented the production of methyl dodecanoate (which can be used as biodiesel) using lauric acid and methanol with a solid acid catalyst of sulfated zirconia using two intensified distillation sequences. In the first sequence, the methanol recovery column follows the reactive distillation column. In the second sequence, the reactive distillation and methanol recovery columns are thermally coupled. Thermally coupled distillation sequences may consume less energy by allowing interconnecting vapor and liquid streams between the two columns to eliminate reboiler or condenser or both. Comparisons of the optimized sequences show that in the thermally coupled sequence, the energy consumption is reduced by 13.1% in the reactive distillation column and 50.0% in the methanol recovery column.

The esterification of a ternary mixture of fatty organic acids (oleic acid, linoleic acid, and N-dodecanoic acid) with methanol catalyzed by sulfuric acid was studied by Cossio-Vargas et al. [18]. A complex reactive distillation column and two thermally coupled distillation columns were simulated considering the reaction inside the column, and the results indicate that the three reactive distillation columns can produce a ternary mixture of esters as bottoms product that can be used as biodiesel. In this particular case study, the reactive thermally coupled distillation with a side rectifier can handle the reaction and the complete separation.

The esterification of lauric acid and methanol is explored using thermally coupled distillation sequences with side columns and with a minimum number of reboilers in the paper by Vázquez-Ojeda et al. [129]. The product of the esterification can be used as biodiesel. This is a major step forward since thermally coupled reactive distillation sequences with side columns and with a minimum number of reboilers offer significant benefits, such as the following: reductions on both capital investment and operating costs due to the absence of the reboilers and higher conversion and selectivity since products are removed as they are produced as well as no occurrence of thermal degradation of the products due to a lower temperature profile in the column.

Kiss et al. [60] propose a novel biodiesel process based on a reactive dividing-wall column that allows the use of only 15% excess of methanol to completely convert the fatty acids feedstock. Fatty acid methyl esters are produced as pure bottom product, water as a side stream, while the methanol excess is recovered as top distillate and recycled. The optimal setup was established by using simulated annealing as an optimization method implemented in Matlab and coupled with rigorous simulations carried out in Aspen Plus. The novel design alternatives allow the reduction in energy requirements by over 25% and by using fewer equipment units than conventional processes.

Esterification reactions of fatty organic acids and a mixture of fatty organic acids with a composition similar to J. curcas L. seed oil with methanol were carried out in a complex reactive distillation sequence and two thermally coupled distillation sequences, obtaining that it is possible to produce esters with a very high composition as bottoms products that can be used as biodiesel [19]. This route of production of biodiesel takes into account process intensification principles; for instance, reductions in energy requirements and reaction and separation in the same unit. Also, the excess of methanol used in the reaction can be recovered in the same reactive complex distillation column.

One of the first studies to tackle the optimal design, dynamics, and control of a highly integrated reactive dividing wall column for Fatty Acid Methyl Esters synthesis, from free fatty acids and methanol is presented by Ignat and Kiss [51]. One of the relevant results of this paper is that it is imperative to use a vapor feed of alcohol to reach the product specifications. Singular value decomposition was used to determine the sensitive trays for inferential temperature control. The control structure proposed demonstrates the excellent performance of the system in the case of industrially relevant disturbances such as production rate changes or catalyst deactivation.

A laboratory-scale dividing wall column to study the esterification reaction of oleic acid and methanol using sulfuric acid as homogeneous catalyst was implemented by López Ramírez et al. [71]. According to experimental tests, the best conditions for the production of Fatty Acid Methyl Esters are molar ratios of methanol/carboxylic acid, reaction time temperature, and catalyst weight. These results are valuable as a preliminary study on biodiesel production, using an acid homogeneous catalyst in a reactive dividing-wall distillation column.

Sakhre et al. [107] propose a novel process integration for biodiesel blend in the membrane-assisted reactive Divided Wall Distillation column. Dual reactive distillation and membrane-assisted reactive Divided Wall Distillation column were simulated using aspen plus. Intensified DWC was compared with a dual reactive distillation column and it was observed that membrane assisted reactive Divided Wall Distillation column is comparatively cost-effective and suitable in terms of improved heat integration and flow pattern

In general, papers show that the reactive dividing wall column technology can be used efficiently for the synthesis of biodiesel, thus simplifying the process flowsheet and drastically reducing the specific energy use while simplifying the processes by using less equipment that requires a lower plant footprint [64],[117].

### 3.3. Other reactive intensified options

A pioneering biodiesel process based on free fatty acids esterification in a reactive absorption column using solid acids as green catalysts was presented in the paper by Kiss [58]. The most favorable results were attained near the stoichiometric reactants ratio and relatively high temperature of the fatty acids feed stream. At optimal operation, the highest yield and purity can be achieved by using a stoichiometric reactants ratio, with a practically negligible amount of methanol lost in the top and complete conversion of the fatty acids.

Su et al., [121] proposed the use of dimethyl carbonate or diethyl carbonate as simultaneous extraction solvent and trans-esterification reagent for the in situ lipase-catalyzed reactive extractions of oilseeds for biodiesel production. Fatty acid methyl esters and ethyl esters were obtained with, respectively, 15.7% to 31.7% higher yields than those achieved by the regular two-step extraction/trans-esterification process. Key parameters such as solvent/seed ratio and water content were also investigated to examine their effects on the in-situ reactive extraction.

Machsun et al. [75] used a biocatalytic membrane microreactor for continuous transesterification by using an asymmetric membrane for immobilizing the enzyme. The performance of biodiesel synthesis from triolein and methanol was studied. Transesterification was carried out by passing a solution of triolein and methanol through the membrane giving a triolein conversion of about 80%. The system displayed good stability, with no loss of catalyst activity over 12 days of continuous operation. The results from the triolein trans-esterification demonstrate the potential of an asymmetric membrane as an enzyme carrier material.

Lim et al. [69] proposed the use of supercritical reactive extraction from Jatropha curcas L. oil seeds as cost-effective processing technology for biodiesel production. Compared with traditional methods, supercritical reactive extraction can successfully perform the extraction of oil

and subsequent simultaneous esterification and trans-esterification processes to free fatty acids in a relatively short time. The particle size of the seeds and the reaction temperature and pressure are the primary factors affecting the process.

Kiss and Bildea [59] used sensitivity analysis to evaluate the range of the operating parameters: reactants ratio, the temperature of feed streams, decanting temperature, flashing pressure, and recycle rates in an integrated reactive absorption process for the synthesis of fatty esters. Results show that the optimal molar ratio of the reactants (alcohol/acid) is very close to the stoichiometric value. In practice, using a very small excess of methanol (up to 1%) or an efficient control structure is sufficient for the complete conversion of the free fatty acids in this kind of configuration.

A novel intensification that improves the pretreatment stage of biodiesel production, which converts problematic free fatty acids to fatty acid methyl esters, by the introduction of a microbubble mediated reactive distillation stage instead of acid pretreatment is presented by Zimmermana and Kokoo [136]. This will shift the conventional esterification process towards completion with a yield higher than 80%, even without high excess methanol. Application of ozone microbubbles has the advantage over acid gas catalysis in that it gives higher conversion and leaves no catalyst residue and requires no further catalyst recovery separation steps. The results also show that the conversion of oleic acid to form oleic acid methyl ester is 91.16% after 32 h of ozonolysis at 60 °C. Therefore, the free fatty acid content in used cooking oil is less than 1.33%, which makes it suitable as a reactant for biodiesel production via transesterification.

In the coming times, there are still important challenges to be addressed in the biodiesel production area via intensified processes. It is still necessary to conduct detailed experimental and economic studies to garner support concerning the simulations done by researchers in particular for reactive distillation. Heterogeneous catalysts from biomass sources stand out as grossly underexplored based on both environmental and economic viability. Great challenges in the area of optimization, under sustainability criteria, of novel and little-explored systems such as membrane reactor process or reactive liquid-liquid extraction are necessary [88]. While the variety of readily available oils has largely been studied to discover the optimum process conditions required to extract the maximum product yield, attention has now must be turned to the less traditional sources of triglycerides, such as algae and other lipids from various sources. The research on processing methods has likewise broadened to include the use of heterogeneous bi-functional catalysts, the use of supercritical methods, and the integration of the biodiesel production process with other co-processes such as power co-generation and biogas production from the digestion of micro-algal waste.

## 4. PI in the biobutanol purification

Except for the use of solvent, chemical intermediate, and extract agent, butanol also can be used as fuel, which attracted people's attention in recent years. Because of the good properties of high heat value, high viscosity, low volatility, high hydrophobicity, less corrosive, butanol has the potential to be a good fuel in the future. Compared with ethanol, butanol overcomes the above disadvantages and shows potential advantages. For example, Butanol has higher energy content and higher burning efficiency, which can be used for long distances. The air to fuel ratio and the energy content of butanol is closer to gasoline. So, butanol can be easily mixed with gasoline in any proportion. Butanol is less volatile and explosive, has a higher flash point, and lower vapor pressure, which makes it safer to handle and can be shipped through existing fuel pipelines. In addition, Butanol can be used directly or blended with gasoline or diesel without any vehicle retrofit [95]. Studies about the intensification of the purification process of this interesting biofuel have less than 10 years in the open literature.

Because of the low concentration acquired from the fermentation broth, which can contribute to high energy consumption during separation and purification procedures, product recovery is a major issue connected with the manufacture of biobutanol on an industrial scale. Long-term stability, excellent selectivity, and a high removal rate are all desirable characteristics in a recovery technique. The development of a homogeneous azeotrope between ethanol and water, as well as a heterogeneous azeotrope between biobutanol and water, adds to the complexity of the purification process.

In pioneering works, van der Merwe et al. [128] and Sanchez-Ramirez et al. [109] study different possible process designs for biobutanol purification from sugarcane molasses. Three of the alternatives presented are based solely on distillation columns (see Fig. 6). In these three schemes presented, the first column is in charge of concentrating the solution coming from the fermentation broth up to the azeotropic point. The second column, depending on the scheme, can be used to obtain acetone or to further distribute the components. Once the components have been redistributed, the presence of the heterogeneous azeotrope is used to obtain a butanol-rich stream using a decanter. Finally, using two final distillation columns, two high purity streams of butanol and water respectively can be obtained. On the other hand, the configuration that ultimately proved to be the most promising is initially configured by a liquid-liquid extraction column. This column, aided by a solvent, can break down the azeotropes present. The organic stream, coming from the extraction column, is separated more simply into three distillation columns, recirculating the solvent. The designs were optimized using a differential evolution algorithm. The results indicated that the process hybrid consisted of a liquid-liquid equilibrium column followed by steam stripping distillation proved to be a probable design in current economic conditions, which was evaluated through total annual cost calculation. Both studies can be considered as a reference case since from those schemes, several designs were further proposed (Fig. 6).

Considering que optimized results from Sánchez-Ramírez et al. [109], the paper by González-Bravo et al. [41] presents an optimization approach for designing energy integrated biobutanol separation processes. The optimization incorporates attractive hybrid separation options using liquid-liquid equilibrium column with different solvents as well as incorporating several options for waste heat recovery involving integrated heat exchanger networks, stream Rankine cycles, organic Rankine cycles, and absorption refrigeration cycles. The results show significant economic and environmental benefits for the simultaneous consideration of the optimization of the separation process with the waste heat recovery for the biobutanol separation process.

Closing the loop regarding the work presented by Sánchez-Ramírez et al. [109] the control properties have been studied on those hybrid systems. The work presented by [3]; analyzed the dynamic behavior of the four alternatives presented by Sánchez-Ramírez et al. [109]. The results, in general, indicate that the intensified systems for the purification of biobutanol tend to present better dynamic performances.

The works proposed by van der Merwe et al. [128] and Sanchez-Ramirez et al. [109], were taken as a basis for the development of various intensification techniques applied to distillation columns, thermal couplings, movement of column sections, inclusion of divided walls, etc. The following sections will discuss the various optimization strategies applied to these base schemes.

Some other separation alternatives based on distillation columns have been presented, for example, a novel downstream process using only several operating units in an optimized distillation sequence including process intensification options such as dividing wall column technology, as well as heat integration that can radically reduce the costs and improve the economics of biobutanol production is presented in the paper by Patrascu et al. [92]. The main improvements include using a decanter as the first unit of the separation sequence avoiding the use of a preconcentration step and preventing phase separation in the stripping and distillation columns, placing the column separating ethanol in the recycle loop of the butanol-water separation to prevent ethanol accumulation. The specific energy requirements for the

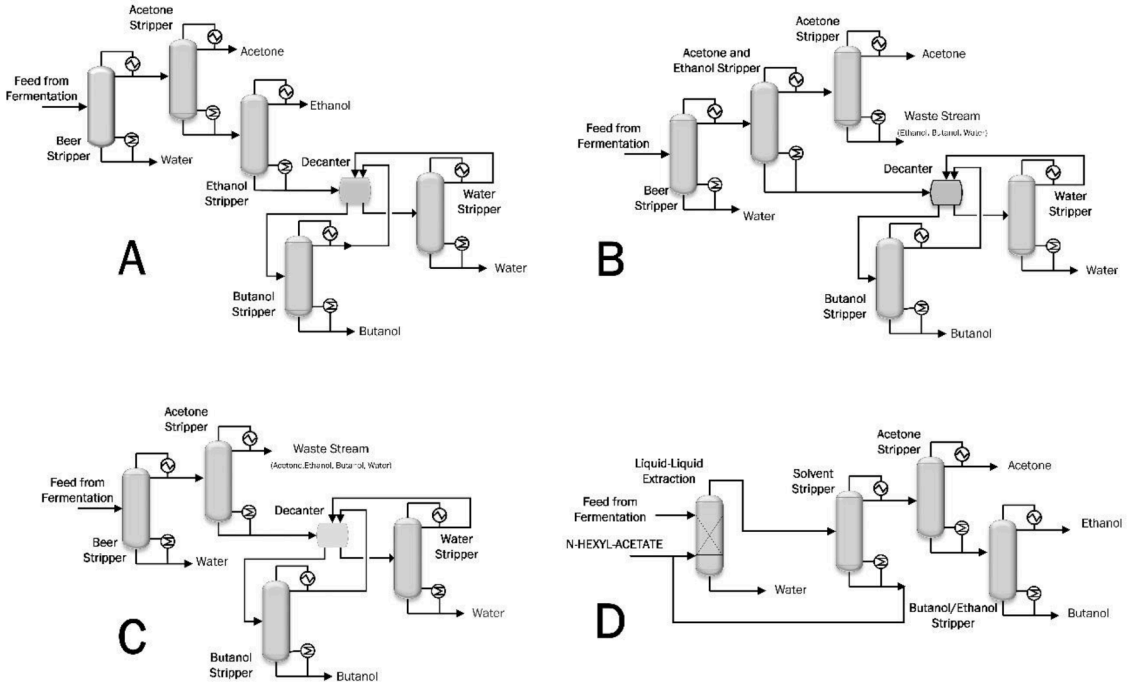


**Fig. 6.** Separation alternatives presented by van der Merwe et al. [128] and Sanchez-Ramirez et al. [109].

separation and purification of butanol are very low (1.24 kW h/kg butanol), especially considering that butanol fuel has an energy density of about 10 kW h/kg. Unfortunately, the latter work was not followed up in terms of process intensification as was the work of van der Merwe et al. [128] and Sanchez-Ramirez et al. [109].

### 4.1. *Thermally coupled alternatives to purifying biobutanol*

Starting from the hybrid process presented in Sánchez-Ramírez [109], novel alternative hybrid configurations based on liquid-liquid extraction and intensified distillation configurations for biobutanol purification were presented in the paper by Errico et al. [26]. The alternatives are designed and optimized minimizing two objective functions: the total annual cost and the eco-indicator 99. All the novel configurations presented reduced the TAC compared to the traditional hybrid con figuration, in particular, a thermally coupled alternative (with two thermal couplings) exhibited a 24.5% reduction of the TAC together with an 11.8% reduction of the environmental indicator. Some alternatives presented by Errico et al. [26] are presented in Fig. 7

Taking the work of Van der Merwe et al. [128] and Sanchez-Ramirez

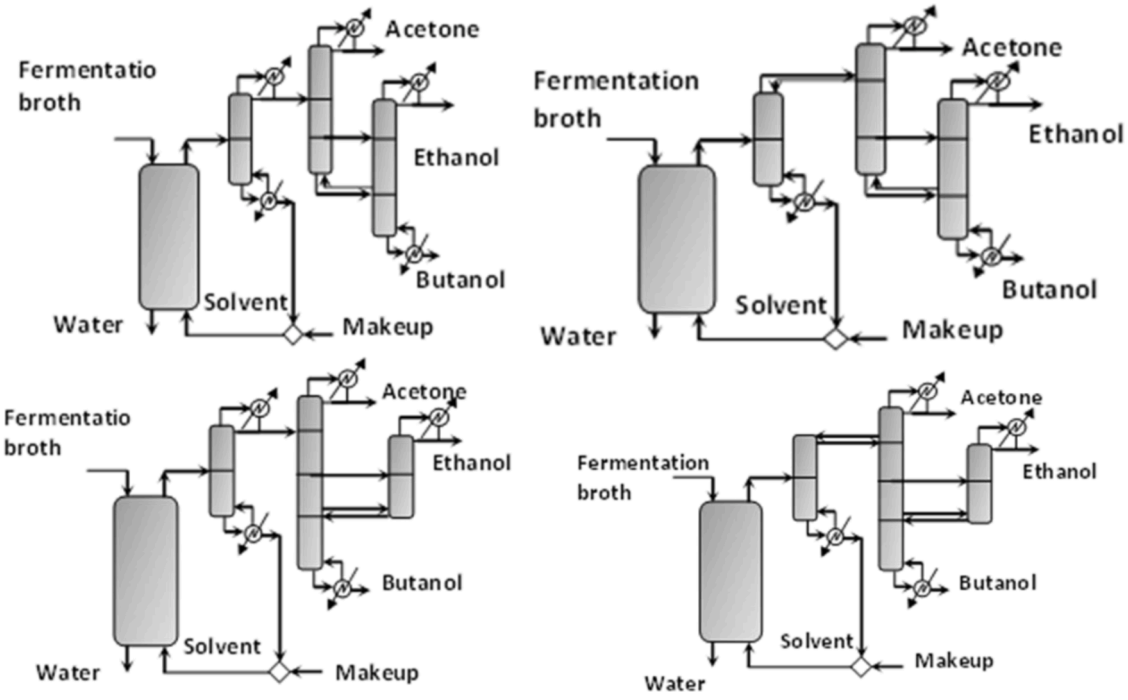


**Fig. 7.** Separation alternatives presented by Errico et al. [26].

et al. [109] as a basis, a proposal for enhancing the purification process of the ABE mixture is presented, in the paper by Contreras-Vargas et al. [17], which implies avoiding the ethanol/butanol separation since this mixture can be used as fuel in internal combustion engines. Design for conventional and intensified distillation trains are presented and optimized in terms of total annual cost and environmental impact, assessing the safety properties of each sequence. The sequences are compared with the previously reported train, in which ethanol and butanol are obtained as separated products, to assess the impact of the proposed modification on the studied indexes. Eliminating the column with the task of separating the ethanol/butanol mixture has only little effect on the total annual cost and the environmental impact since the column with the highest energy requirements is the one that recovers the solvent used to remove the water in the ABE mixture. Nevertheless, the reduction in the number of columns has a high impact on the safety of the process.

### 4.2. Dividing wall-based alternatives to purifying biobutanol

After analyzing the results generated including thermal couplings, the work by Sánchez-Ramírez et al. [110] was the first to report the use of hybrid separation based on liquid-liquid extraction combined with dividing wall column technology for the purification of the ABE mixture. The proposed configurations are the result of multi-objective optimization that aims to find designs that will fulfill the tradeoff between those objectives: cost minimization, reduce environmental impact, and increase controllability. The scheme containing a dividing wall column thermally coupled to a conventional distillation column shows the most balanced design among the four schemes evaluated, as it showed the lowest total annual cost values, as well as good values in environmental impact and dynamic behavior.

In the same way as Sánchez. Ramírez et al. [110], the paper by Errico et al. [27], a complete set of dividing wall columns are presented and compared considering a multiobjective function obtained by the combination of three different indexes taking into account the economy, the environmental impact, and the controllability of the alternatives. The alternatives developed (see Fig. 8) took as base the previous work presented by Errico et al. [27]. The alternatives were compared to the liquid-liquid extraction-assisted simple column distillation. In the best configuration selected, the extract stream is fed to a dividing wall column equipped with two reboilers and a side rectifying stream. For this configuration, a reduction of 22% of the total annual cost and 18% of Ecoindicator 99 was observed together with good dynamic behavior. The configurations proposed have been never considered for the ABE separation, and it represents a concrete possibility to improve the competitiveness of the biobutanol process.

On the other hand, Segovia-Hernandez et al. [115] studies ten hybrid and intensified configurations, based on the liquid-liquid extraction and dividing wall columns, to purify the butanol to the fuel grade. The presented work does not offer new butanol separation alternatives, rather it extends the study of separation alternatives previously presented by [27]. The study analyzes sustainability based on green metrics, including the inherent safety and control properties using singular value decomposition analysis. The results indicate that as long as the

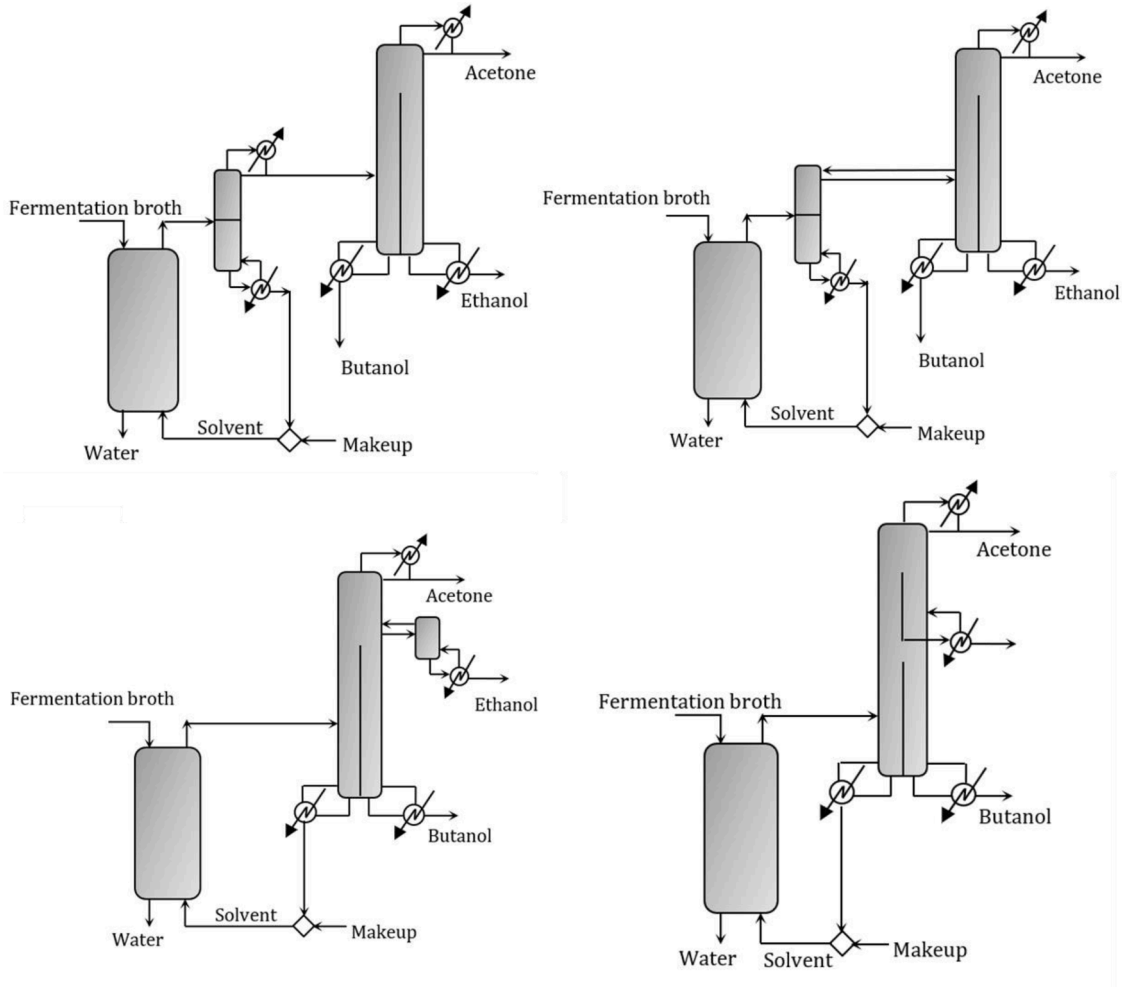


**Fig. 8.** Separation alternatives presented by Errico et al. [27].

process is highly intensified, the sustainability and the inherent safety are improved and not necessarily the control properties. This is primarily due to the loss in the degrees of freedom in intensified processes.

### 4.3. Separation alternatives including a reactive stage to purify biobutanol

Independently of the separation work previously shown, efforts have been made to consider a complete and integral butanol production process. For example, in the work by Quiroz-Ramírez et al. [102] has been simulated and optimized a process to produce acetone, butanol, and ethanol employing lignocellulosic material. To accomplish this task was planned the raw material selection, followed by the simulation intensified simultaneous saccharification, fermentation, and separation reactor, and finally, the stream coming from fermentation was purified by analyzing three intensified separation systems. The entire intensified process was evaluated under an optimization process considering environmental, economic, and energetic objective functions using a hybrid stochastic method. The obtained results showed that the best scheme to produce and purify butanol that considers thermally coupled columns all the products generated in the fermentation process.

Sánchez-Ramírez et al. [111] propose purification schemes to obtain butanol of high purity, from a butanol-water mixture, in the compositions generated by reduction of volatile fatty acids, using pervaporation, pressure swing distillation, and azeotropic distillation (see Fig. 9). The evaluation of the sustainability metrics was carried out through the multiobjective optimization of the model using four objectives together: total annual cost, environmental impact, inherent safety, and control properties. The pervaporation scheme turned out to be the most promising alternative.

### 4.4. Other intensified to purify biobutanol

Butanol can be produced through ABE fermentation, but the production cost is still relatively high due to its very dilute concentration. Separation of butanol from ABE fermentation broth is very challenging and critical for successful commercialization. Therefore relevant challenges must be explored for the near future. Integration of ABE fermentation with a product recovery process such as gas stripping, vacuum flash, solvent extraction, perstraction, membrane pervaporation, thermopervaporation, and adsorption, as process intensification, can efficiently eliminate product inhibition, enhance cell growth, increase productivity and, and hence could reduce energy consumption and downstream separation cost and make the overall system more viable [50].

Friedl [32] studied three different hybrid separation processes, namely liquid-liquid extraction and pervaporation with distillation and a novel adsorption/drying/desorption hybrid process. Compared with the energy content of butanol, the energy necessary for butanol separation were 11 – 22% for pervaporation/distillation, 11– 17% for liquid-liquid extraction/distillation, and 9.4% for a novel hybrid adsorption/drying/desorption process.

Based on a comprehensive review of the literature and comparison of the various separation and purification technologies, it is concluded that membrane pervaporation, L-L extraction, and adsorption are the most energy-efficient approaches for the removal of butanol from the ABE fermentation products. Improvement of membrane technologies, especially the development of thin membranes with higher flux, higher separation factor, increased strength, and high stability, as well as antifouling characteristics or better cleaning technologies, etc. still need to be explored. For L-L extraction, novel extractants are still needed to be developed with the aid of molecular modeling techniques and chemically modifying its affinity to butanol or hydrophobicity. For adsorption method, modification of current high performing adsorbents, study on adsorbent fouling problems and stability of adsorbents, methods for efficient desorption or adsorbent regeneration with a high concentration of butanol are also worthy of further exploration. In addition, these three

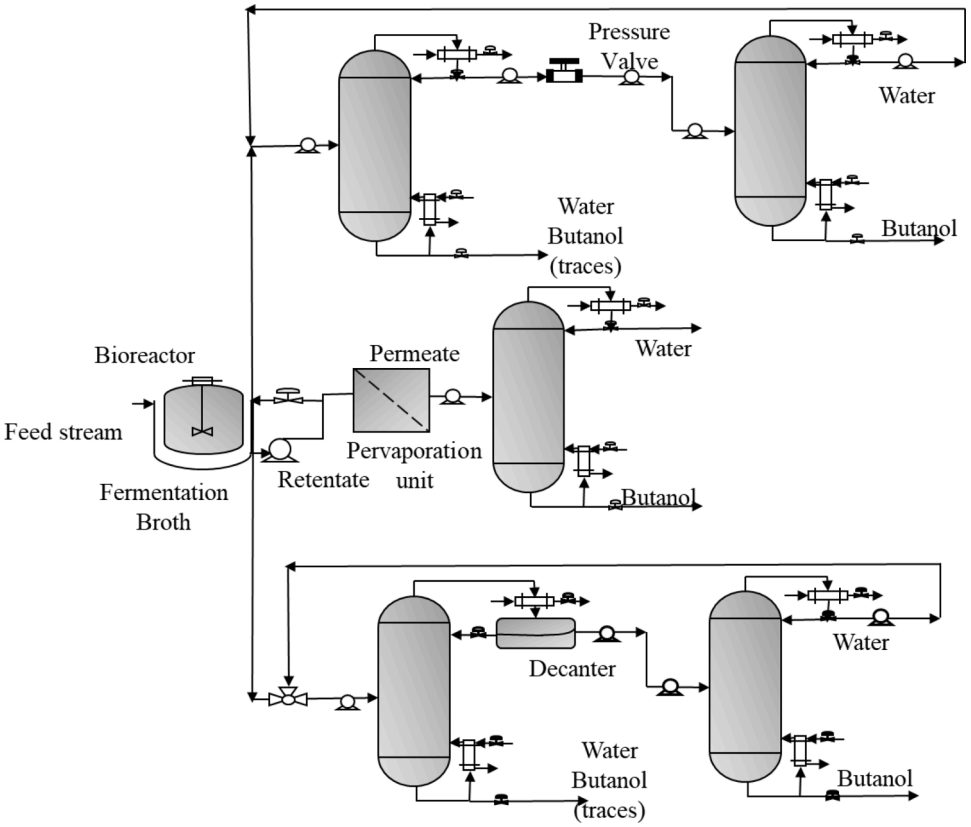


**Fig. 9.** Separation alternative for biobutanol from fatty acids.

hybrid separation processes incorporated with fermentation as a whole system need to be optimized [24].

An alternative separation process including reactive distillation columns is proposed to purify biobutanol from acetone-butanol-ethanol fermentation in then paper by Kaymak [55]. As a result of the reaction taking place in the process, ethylene glycol is obtained as an added-value coproduct besides the purification of butanol. The steady-state simulations indicate that the total annual cost decreases significantly when compared with flowsheets given in the literature based on extraction L-L and distillation. Effective control structures are designed and their robustness is tested against two different types of load disturbances in the intensified configurations.

Finally, it is important to note the energy that some authors point out was considered to purify the butanol produced. Table 3 shows some summarized data on energy requirements. On the other hand, some specific data can also be found in the literature. For example, a hybrid gas stripping/distillation process (from 0.78 wt percent to pure) requires 21 MJ/$kg_{Butanol}$ [50]. For gas-stripping/distillation, several publications indicate energy demands ranging from 14 to 31 MJ/kgButanol [15]. A newly reported gas-stripping/pervaporation/distillation hybrid method (1 wt% to >99.5 wt%) necessitates 23 MJ/kgButanol [15]. A new dual extraction/distillation (from 2.2 wt percent ABE to 92 wt percent ABE) technique for liquid-liquid extraction has been proposed, with energy consumption for producing an ABE product combination as low as 4 MJ/kgButanol [66]. Other studies confirm this number, citing a value of 5 to 6 MJ/$kg_{Butanol}$ for butanol separation from 0.8 wt% to 99.5 wt% [50]. The separation and concentration of butanol from 2 wt percent to 98 wt percent need only 3.4 MJ/kg Butanol for a silicalite sorbent, according to experimental study and modeling of a new adsorption/-drying/desorption hybrid method [4]. Pervaporation is the most researched of the membrane processes, and it is by far the most developed separation technology. With 4 (1 wt percent to pure; Negishi et al. 2014[83]) and 8.2 MJ/$kg_{Butanol}$ (0.5 wt percent – 99.9 wt percent; [74]), the hybrid pervaporation/distillation method is used.

## 5. PI in the biojet fuel purification

Biojet fuel has become a key element in the aviation industry's strategy to reduce operating costs and environmental impacts. This jet fuel must meet ASTM International specifications and potentially be a 100% drop-in replacement for current petroleum jet fuel. The main challenges for the technology pathway are conceptual intensified process design, process economics, and life-cycle assessment of greenhouse gas emissions. Although the feedstock price and availability and energy intensity of the process are significant barriers, biomass-derived jet fuel has the potential to replace a significant portion of conventional jet fuel [132]. It is important to highlight that studies on the intensification of the biojet fuel production-purification process are an area little explored and with large areas of opportunity. Few studies have been reported to date.

**Table 3**
Energy requirements for biobutanol purification.

| Feed Stream (water+ethanol) | Energy requirements (MJ/kg ethanol) | Separation Technology | Reference |
|---|---|---|---|
| 100 lb mol (A: 16.95% wt B: 30.18%wt E: 0.73%wt W: 52.14% wt) | 58.72 | Distillation and hybrid liquid-liquid/ distillation | Sanchez-Ramirez et al. [109] |
| 100 lb mol (30.18% B, 16.95% A, 0.73% E, 52.14% W) | 78.56 | Thermally coupled distillation columns | Errico et al. [26] |
| 100 lb mol (30.18% B, 16.95% A, 0.73% E, 52.14% W) | 71.48 | Dividing Wall Colum | Sánchez-Ramnírez et al. [110] |
| 26,945 kg/h (A: 4.5%wt B: 18.6%wt E: 0.9%wt W: 75.9% wt) | 6.16 | Decanters and distillation columns | Patrascu et al. [92] |
| 100 lb mol (30.18% B, 16.95% A, 0.73% E, 52.14% W) | 61.49 | Dividing Wall Colum | Errico et al. [27] |
| 26,945 kg/h (A: 4.5%wt B: 18.6%wt E: 0.9%wt W: 75.9% wt) | 4.22 | Reactive Distillation Columns | Kaymak [55] |
| 281,980 kg/h (A: 12.3% wt B: 29.1%wt E: 0.62%wt W: 57.98% wt) | 33.66 | Thermally coupled distillation columns | Quiroz-Ramírez et al. [102] |

Dodecane is a product that has received increased commercial interest quite recently as a possible surrogate for kerosene-based fuels such as Jet-A, S-8, and other conventional aviation fuels. the possibility of using reactive distillation for dodecane production. In Gaurav's doctoral thesis (2017) preliminary results suggested that reactive distillation presents an excellent opportunity to produce dodecane. This means an opportunity to intensify intermediate zones in the biojet fuel production process and thus generate more sustainable and economically profitable processes.

The immediate application of intensification techniques occurred in a paper presented by Romero-Izquierdo et al. (2020). In their work the modeling and simulation of the alcohol-to-jet fuel (ATJ) conventional process is presented considering as raw material bioethanol produced from lignocellulosic wastes (see Fig. 10). The effluent from the co-fermentation reactor, which is part of the bioethanol production process using lignocellulosic wastes as raw material, provides the feedstock for the ATJ process. 257,673 kg/h of bioethanol is used to make this effluent, which also contains traces of glycerol, water, and ammonia. Dehydration, oligomerization, and hydrogenation, as well as a separation zone, are all part of the ATJ process. The bioethanol is dehydrated at 450 °C and 11.4 bar in the first reactive step, with saturated steam, added to achieve 99.5 percent ethylene conversion. The RStoic module in Aspen Plus simulates this reactive stage. The ethylene produced in this reactive step is fed into a turbine, which reduces the stream pressure to 3 bar. This pressure is required to separate the ethylene in a distillation column with a partial vapor-liquid condenser designed to recover 99 percent of the ethylene, as illustrated by a RadFrac module. The recovered ethylene is injected into the second reactive step, oligomerization, which runs at 120 °Celsius and 35 bar. The RStoic module in Aspen Plus is used to model this reactor. The oligomerized products are fed into the third reactive stage, which runs at 100 °C and 15 bar of hydrogen until 99 percent of the paraffin has been converted. The RStoic module in Aspen Plus models this reactive stage. Renewable hydrocarbons from the last reactive stage pass via a turbine, which lowers the pressure to 1 bar before being sent to the separation zone. To reduce the energy requirements and the environmental impact, process intensification tools are applied to the separation zone, followed by the energy integration of the whole process. The ATJ conventional and intensified-integrated processes are assessed by the total annual cost and the $CO_2$ emissions. The intensification on the separation zone allows reducing energy requirements by 5.31% in contrast to the conventional sequence; moreover, the energy integration of the intensified process reduces by 34.75% and 30.32% the heating and cooling requirements, respectively; as consequence, total annual cost and $CO_2$ emissions are decreased when compared to the conventional process.

Efforts have been made to model and simulate a complete plant for biojet production, for example, Gutiérrez-Antonio et al. [44],[45] presented the modeling of conventional and intensified hydrotreating process to produce biojet fuel. At 480 °C and 80 bar, the renewable hydrocarbon stream exits the reactive section, which is a high-pressure condition for a stream that will be supplied to a distillation train. As a result, a turbine is utilized to condition the stream prior to supplying it to the distillation train; also, the turbine will allow the operation to generate electrical energy. After the hydrocarbon stream's pressure is reduced, it's sent into a distillation train, where it's separated into four

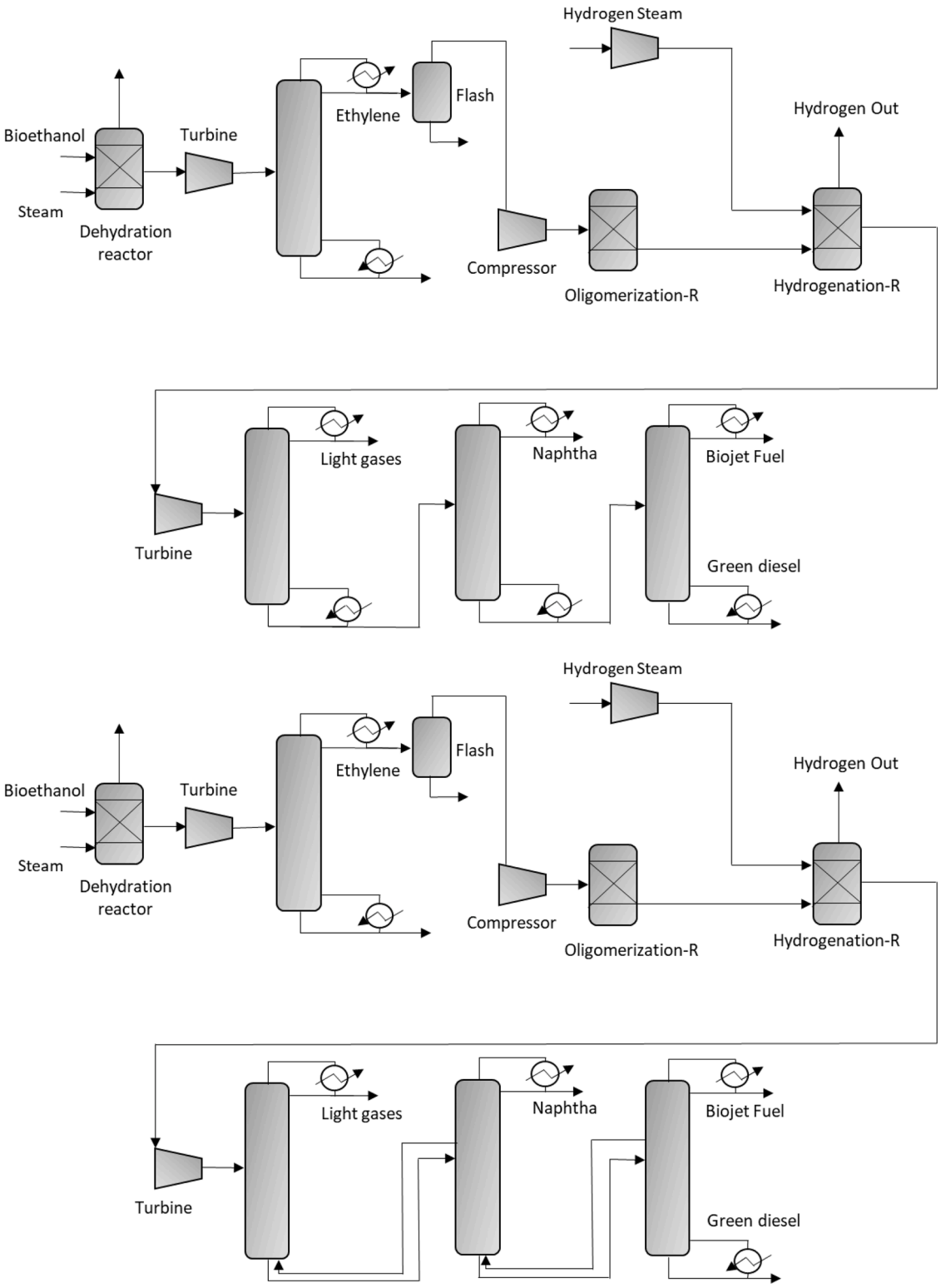


**Fig. 10.** Conventional and intensified processes presented by Romero-Izquierdo et al. (2020).

products: light gasses ($C_1$—$C_4$), naphthas ($C_5$—$C_7$), biojet fuel ($C_8$—$C_{16}$), and green diesel ($C_{17}$—$C_{21}$). These products may be separated using five distillation sequences using conventional distillation (see Fig. 11). The separation of the light components, on the other hand, necessitates the use of refrigerant as a cooling service; as a result, all sequences in which the light gasses were not acquired in the first distillation column are removed. They also recommended a partial condenser in the train's first column to reduce refrigerant usage. As a result, they only evaluate two distillation methods: direct and direct-indirect. For all the hydrotreating processes jatropha curcas and microalgae oils are considered renewable raw materials. The results show that the total annual costs of all hydrotreating processes are similar. However, the $CO_2$ emissions of the conventional structure are 34% higher than the ones reported for an intensified alternative process. Thus, the intensified hydrotreating allows producing biojet fuel with minimum environmental impact and a competitive price, concerning fossil jet fuel.

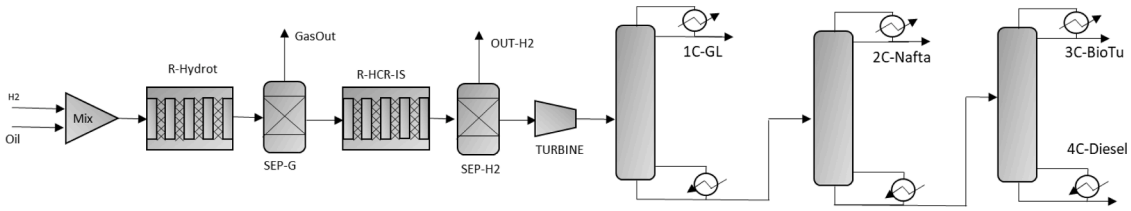


**Fig. 11.** Conventional process to produce biojet fuel.

Similarly, other types of raw materials have been considered for biojet production, e.g. chicken fat. Moreno-Gómez[80] presented the modeling, simulation, and intensification of the hydroprocessing of chicken fat to produce renewable aviation fuel. For this, conventional hydrotreating processes are modeled and used to define the intensified ones, where complex configurations are used to perform the purification. All processes are compared in terms of economic and environmental indicators. Results show that the best scenario in terms of economic and environmental indicators is the process that includes conditioning and reactive zones along with a direct intensified sequence; in this scenario, there is the best trade-off between the price of biojet fuel and the carbon dioxide emissions.

Among the proposed processes for the production of renewable jet fuel, the hydrotreating process has the best performance. At the final stage of the hydrotreating process, a distillation train is required to obtain hydrocarbon fractions useful as fuels. Conventional and intensified coupled distillation sequences can be used in this step, and it can be expected that intensified sequences require less energy to perform the separation. Different cases, from the low- to the high-duty regions of the Pareto front, were selected and studied through open-loop and closed-loop methods in the paper by Acosta-Solórzano et al. [1]. The open-loop results and the closed-loop results give detailed information on the dynamic performance of the systems. Intensified systems have the lowest energy consumption and the best dynamic properties, which is an indication that intensified distillation systems, for the production of renewable jet fuel by the hydrotreating process, is a possible option for industrial implementation.

### 5.1. *Intensification in reactive stages to produce biojet fuel*

In addition to the intensification applied to the separation section, some works oriented to the intensification of the reaction zone have been presented. For example, an intensified three-step hydrotreating reaction-separation process for the production of bio-jet fuel from triolein and petrodiesel mixtures has been developed in the work by García-Sánchez et al. [34]. Through intensive simulations, the effect of different operating variables (triglyceride-water feed ratio, oleic acid-petro-diesel feed ratio, hydrogen consumption) on the performance of the intensified reactive separation process was studied. it can be highlighted that the key design and operating parameters for the production of the biojet fuel are: the water excess and the total pressure for the heterogeneous catalytic hydrolysis reactor and if high molar flows of fatty acid are considered, it is mandatory to have more reactive stages in a reactive distillation column to achieve ultra-clean (no-sulfur) petro-diesel at the bottom of the column.

In one of the most complete books to date about the production of Biojet fuel, Gutierrez-Antonio et al. [46] present the application of intensification and energy integration strategies for the production of renewable aviation fuel. The authors indicate that intensification will be one of the most viable strategies for the design of economically profitable and sustainable processes for the large-scale production of Biojet fuel from various biomass.

### 5.2. *Other intensified studies to produce biojet fuel*

A CFD-based model of a sieve tray with catalyst containers working under the operating conditions of a column used for the production of biojet fuel through reactive distillation was developed in the paper by Quiroz-Pérez et al. [100]. The model was used to analyze the effect of the geometric design of both sieve tray and catalyst containers on the system performance. The proposed model can serve as a basis for the development of a CFD modeling strategy to evaluate the performance of different tray designs with a similar catalyst configuration for the production of renewable aviation fuel. In this case, mass transfer and chemical kinetics should be incorporated to obtain an appropriate representation of other important phenomena in reactive distillation, such as phase change, diffusion, the heat of vaporization, heat of reaction, etc. Thereby, the contribution of these phenomena on the temperature distribution, turbulence behavior, among others, could be determined.

Today there are still few research and development works focused on Biojet fuel production processes. The research groups have taken two directions: the first direction is focused on the search for efficient catalysts with high selectivity towards Biojet fuel; while the second direction aims to reduce energy consumption during the process by intensifying processes and energy integration. The opportunities are vast in the area, so important contributions are looming soon: economic profitability, environmental impact, energy consumption, inherent safety, dynamic behavior, for example. Biojet fuel is the promising renewable fuel to at least partially replace fossil-based jet fuel and has the potential to reduce the environmental impact of the aviation industry [53]. However, its cost is high compared to that of conventional jet fuel. It is, therefore, necessary to find intensified alternatives in the different areas of the process to reduce production costs.

## 6. Future trends

In the past decade, we have seen technological advancements in motor vehicles that run on renewable energy sources. The increasing threat of fossil fuel depletion coupled with the need to maintain renewable sources continues to push for the demand for biofuel. We live in a world where the global market for biofuels and renewable sources continues to grow to maintain the growing population. Reliance on energy is a global necessity as the government attempts to mitigate the growing issue of climate change as a direct result of increased demand for automobile fuel. The most obvious benefit of replacing fossil fuels is the environmental impact it will have on carbon emissions. Since biofuels burn faster and cleaner than fossil fuels, they will release greenhouse gasses at a lower rate. Secondly, the use of biofuels will allow the economy to reap its benefits.

One of the main focuses of this review is the future of the purification of four main liquid biofuels. As noted throughout this paper, this clearly defines the grand challenge in the production and purification of liquid biofuels, which is the production of more fuels but with significantly lower carbon emissions, minimum energy consumption, and economic profitability. An important relationship exists between the design and operation of upstream catalysis units and downstream separation systems. Producing more liquid biofuels with lower carbon emissions will require energy-efficient capacity additions. Advanced separations play a

significant role in this regard. First, advanced separations such as membranes and adsorption are thermodynamically advantaged relative to traditional separations such as distillation and absorption. However, traditional separation systems provide fundamental advantages in terms of product purity and recovery, as equilibrium stages can be added with minimal additional energy costs whereas the advanced separation systems often require substantial additional energy inputs for each new stage. Beyond energy, there are capital cost scaling advantages inherent in distillation column design and construction. However, limits exist on column diameters and hydrodynamics, and these limitations contribute to the inflexibility of throughput expansion for distillation. These factors suggest that the path forward involves the hybridization of existing separations technology with incremental capacity additions in the form of advanced separations systems [70]. Process Intensification seems to be one of the most viable strategies for the generation of advanced separation systems that allow the production and purification of biofuels sustainably. Process intensification is a rapidly growing area within chemical engineering, and one of the key unit operations thought to intensify chemical processes is the reactive separator (e.g., a membrane reactor, reactive distillation, reactive L-L extraction). These all-in-one operations have advantages in certain applications such as breaking equilibrium limitations and a smaller overall footprint.

In particular, for facilitating reproducible results and accurate comparison, and eventually leading to industrial adoption, the following generalized guide (based on the one proposed by [119]) is suggested for future papers on the production and purification of biofuel liquids using intensified processes:

a) State liquid biofuel production rate and its purity, thermodynamic models, and their parameter values used. Also indicate values of temperature, pressure, and composition for all streams in the process flow sheet.
b) Simulate the process as realistically as possible starting. Try to use real mixtures, with compositions as close to reality. In the case of simplified mixtures, justify the reason appropriately.
c) For sizing and costing, follow the procedures in Turton et al. [127] which are detailed and relatively recent. Update estimated costs using CEPCI (Chemical Engineering Plant Cost Index).
d) Costs for adsorbent, membrane replacement, makeup solvent, and others, if any, must be included. If some costs are not considered, the reason why they have not been included must be justified.
e) If the total annual cost is evaluated for economic analysis, then a reasonable payback period of 3 to 5 years should be considered. It is also essential to include investment cost, operating cost, fixed manufacturing cost, and general expenses.
f) Present thermal energy (reboilers, heaters, and steam turbine-driven compressors, etc.) and electricity (e.g., for motor-driven compressors and pumps) separately.
g) Present values of energy (for reboilers and compressors) and separation cost, both per kilogram of biofuel produced.

A relevant point to comment on is the experimental part and the commercial production of liquid biofuels. Several studies have highlighted several bottlenecks that are being faced by big corporations (from experimental part to commercialization) in liquid biofuel production technology (pretreatment, hydrolysis, microbial fermentation, and biofuel separation). Big corporations and oil companies that have the capital to establish a new biorefinery are currently trying to align different novel process technologies that still have several separation and purification challenges to overcome [77]. The use of intensified processes opens up an excellent opportunity for the generation of liquid biofuels in a sustainable way and in accordance with the principles of the circular economy. The choice of pretreatment and lignocellulosic biomass could be decided based on the availability of a sufficient quantity of catalyst and feedstock. The aligned technologies are currently scaled up to establish pilot plants to demonstrate the feasibility. Simultaneously, biomass logistics and techno-economic evaluations are carried out to assess the technology readiness level [120]. Then assessments are made regarding the environmental impact of using different technologies. Once appropriate feedstock, pretreatment, and enzymes are combined to produce cheap sugars, the choice of biofuels and biochemicals depends on the market demand and more importantly the biofuel policy defined by the local and federal government. Furthermore, to compete with the cost of petroleum fuels, the cost of biofuel processing should be kept as low as possible using energy-efficient technologies and using less water. Producing as many coproducts as possible in a biorefinery will help to reduce the cost of biofuel production. If favorable conditions prevail after overcoming these hurdles, then a high capital of about 200–300 million dollars is required to establish a commercial-grade biorefinery that could produce several million gallons of liquid biofuels per year [77].

Finally, the COVID19 pandemic caused a drop of 8.5% in global transport fuel use in 2020 concerning the previous year due to restrictions on people's movements and disruption in trade logistics around the globe. Consequently, biofuel use fell by 8.7% in 2020 concerning 2019 feedstock (OECD-FAO Agricultural Outlook 2021–2030). Once the new normal (post-pandemic) is installed, global biofuel use is expected to grow in the next 10 years. Blending mandates (mixtures fuels-biofuels) are expected to evolve over the projection period for some emerging economies. However, the projection is expected to remain below the E20 goal the government seeks to achieve by 2030. Global biofuel production will continue to be supplied predominantly by traditional feedstock (OECD-FAO Agricultural Outlook 2021–2030 [86]). The major risks and uncertainties for the future development of the biofuels sector are related to the policy environment and oil prices. Policy uncertainty includes changes in mandate levels, enforcement mechanisms, investment in non-traditional biofuel feedstock, tax exemptions and subsidies for biofuels and fossil fuels, and electric vehicles technology and policies for its promotion. In general, new intensified alternatives for biofuel liquid separation should be studied on a consistent and comprehensive basis for accurate comparison. Developing hybrid processes and also intensified technologies will help pave a sustainable path for biofuel production, given that due to the drop in demand due to the COVID19 pandemic, once the new post-pandemic normality is achieved, an increase in the production of liquid biofuels will be necessary to cover in different industrial and automotive sectors.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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